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13. SUPPLEMENTARY NOTES

14. ABSTRACT

We have investigated fundamental aspects of the fracture and deformation behavior of ordered intermetallics (aerospace alloys) on the basis of the ab-initio determination of the parameters needed for further (i) model theoretical, (ii) band structure and (iii) chemical bonding analyses. The research was targeted at investigating the microscopic mechanisms governing the deformation and fracture behavior of intermetallic alloys in order to contribute to the development of a fundamental basis for computer-aided alloy design. Progress in this complex area required understanding such key phenomena as dislocation structure and mobility, and crack blunting and propagation: one most important and challenging component of our research was to bridge the gap between a microscopic quantum-mechanical description of the chemical bonding and the mesoscopic phenomena which govern the mechanical response of intermetallics. Especially for intermetallic compounds and metals of interest, we concentrated on (i) fundamental aspects of dislocation structure and mobility; (ii) solid-solution hardening problems in the context of the fundamental aspects of impurity-dislocation interaction theory; and (iii) the electronic structure of dislocations and related properties of real crystals. The use of a hierarchy of methods was required. Hence, we focused on the application and further development of both state-of-the-art band structure and real-space large scale cluster electronic structure methods, and provided important parameters for atomistic simulations and model mesoscopic simulations.

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BONDING, ENERGETICS AND MECHANICAL PROPERTIES OF INTERMETALLICS

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Abstract

Background

In high-temperature intermetallics, dislocations play an especially important role for understanding mechanisms of their deformation and fracture behavior and anomalous mechanical response which are still far from being well understood and remain a challenge to theoretical explanation. Progress in this complex area requires understanding such key phenomena as dislocation structure and mobility, and crack blunting and propagation: while they have been characterized by mesoscopic length and energy scales, they are determined on the microscopic level by the electronic structure which has, in many cases to be carefully taken into account using ab-initio techniques.

Objectives

The most important and challenging component of our research objectives is to bridge the gap between a microscopic quantum-mechanical description of the chemical bonding and the mesoscopic phenomena which govern the mechanical response. It is highly desirable that theory describes dislocation core structure in a compact and physically transparent form which would provide a natural link with larger length theories of dislocation motion processes (kink formation, propagation and cross-slip) as well as to study how dislocations, as typical extended defects, influence functional properties.

Basic research issues and approach

Our research is targeted at investigating the microscopic mechanisms governing the deformation and fracture behavior of intermetallic compounds. We concentrate on the following key problems specifically for intermetallic compounds and metals of interest: (i) dislocation structure and mobility; (ii) evolution of dislocation structure under different stress conditions; (iii) dislocation core structure in $L1_2$ intermetallics in the context of understanding their anomalous mechanical respo_nse (in relation with HREM measurements in Prof. K. Hemker's group); (iv) features of electronic structure of dislocation and its interaction with point defects. We focus on the application and further development of the combined "continuum/atomistic" description in a form of the highly tractable Peierls-Nabarro (PN) model. This approach allows to treat the mesoscale nature of dislocations in a most natural way and to provide a physically transparent description of dislocation structure that is suitable for use with larger length scale modeling.

One of the most important initial steps is to reliably describe dislocation core structure and its delicate dependence on interatomic interaction/electronic structure. An important feature of a dislocation as mesoscopic object is that atomistic features of the core have to be described along

with long ranged elastic fields - a feature that is more naturally treated within the continuum description.

To parameterize the 2D PN model, we employ highly precise band structure techniques, namely the FLMTO and FLAPW methods. These allow one to perform modeling of dislocation structure on the solid basis of interatomic interactions carefully characterized from electronic structure calculations. Using information on the atomistic structure of the dislocation core we: (i) model other properties of dislocations to establish links with larger scale processes (cross-slip, kink migration) and (ii) calculate the electronic structure of dislocations for a specific material to establish the basis for understanding how these defects influence properties. This methodology is illustrated schematically in Fig.1 showing that the modeling approach is based on ab-initio total energy and interatomic force calculations with that microscopic information used for larger scale modeling within the PN model. Results of these calculations of the dislocation structure are used in two distinct directions for further theoretical analyses.

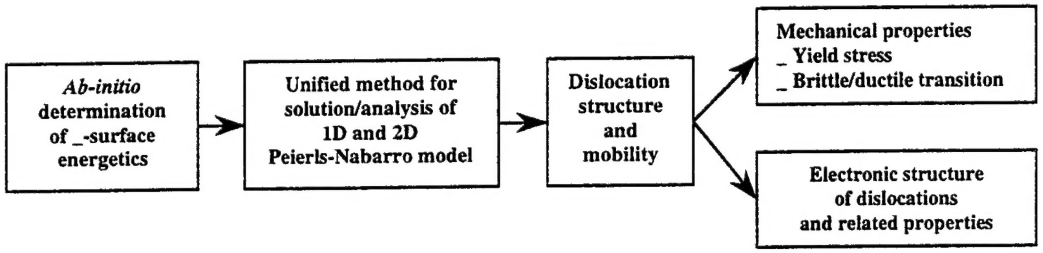

Figure 1: Schematic representation of approach for modeling dislocation structure and related properties starting from first-principles.

Recent research findings

An important part of our research is the development of new functionalities and improvements in the efficiency and accuracy of electronic structure methods and the PN model. We extended the Peierls-Nabarro model to eliminate the "continuum" approximation for the misfit energy, and use it to analyze features of dislocation structure and the evolution of the dislocation core structure under various stress conditions originating in lattice periodicity/discreteness. This extension of the PN model allows one to overcome a critical approximation of the modeling that lattice periodicity effects are neglected in the determination of dislocation core structure. This approximation results in evident inconsistency that the structure of the core in the original PN model is invariant in respect to arbitrary translations [1]. To overcome this inconsistency, while keeping the transparency of the solution comparable with the original simplified model, we proposed a method based on minimization of the total energy functional with Lejcek [2] type trial functions [3].

1. Physically transparent method for solving the PN model with discrete representation of the misfit energy: New features of dislocation structures arising from lattice discreteness.

An appealing feature of the Peierls-Nabarro (PN) model framework in addressing this problem is its high tractability. There is however one critical approximation that limits the predictability of the original PN model, namely, the "continuum" approximation employed to estimate the misfit energy (which itself arises from lattice discreteness). This results in an evident inconsistency and

is considered a serious limitation of the original PN model [1].

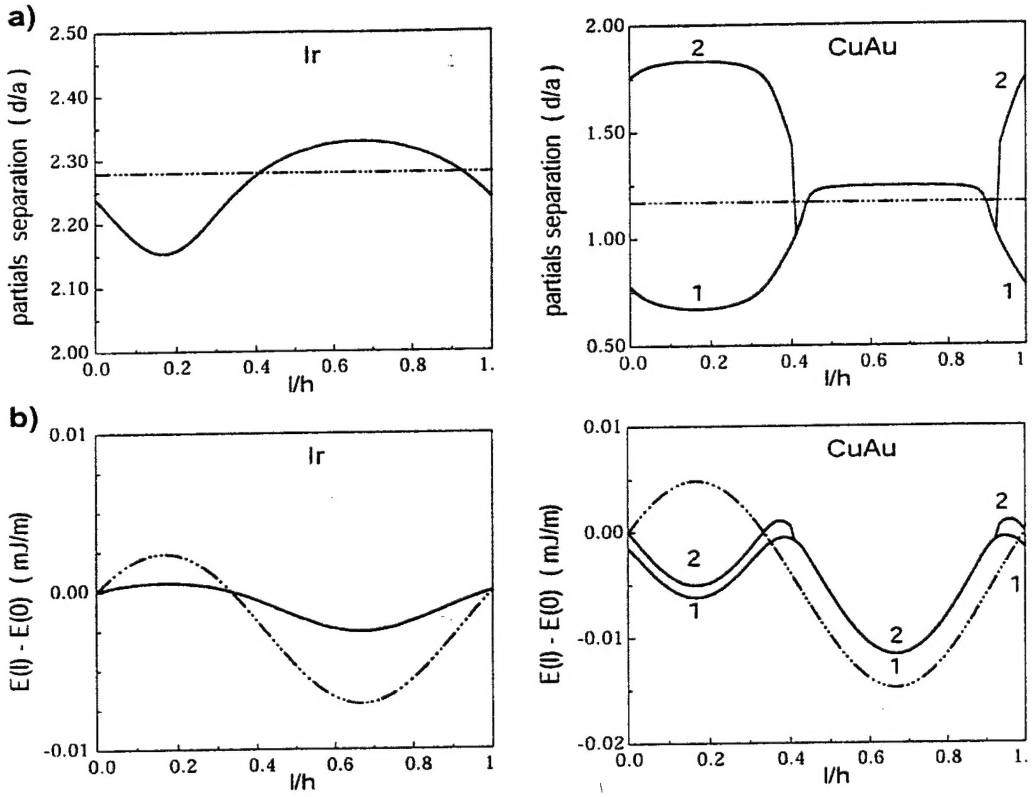

Figure 2: (a) Partials separation, *d*, and (b) dislocation energy (in *J/m)* as functions of the dislocation axis position given by the variable *l* (in units of a repeat distance in the direction normal to the dislocation line *(h))*. Results for the ordinary screw dislocations for Ir (left panel) and CuAu (right panel) with a discrete representation (solid lines) and "continuum" representation (dotted-dashed lines) of the misfit energy. For more than one stable core configurations which are close in energy, the numbering '1' and '2' is used.

Recently, we proposed a procedure which allows one to overcome this inconsistency in calculating dislocation structure. The method has one appealing feature - it represents solutions in a convenient transparent form since the dislocation energy functional can be represented as

$$E_{tot} = E^0_{tot}(d,\omega) + A(d,\omega)\cos\frac{2\pi\, l}{h}\cos\frac{\pi\, d}{h}, \qquad (1)$$

where the *l*-independent first term $E^0_{tot} = E_{el} + E^0_{mis}$ is the energy in the "continuum" approximation and the second term depend explicitly on the lattice parameters *l* and *d*. This feature allows a natural study of how dislocation structure depends on the position of the dislocation axis. In particular, by considering ordinary dislocations in fcc systems with different amplitudes of the Peierls potential we find that dislocation core structure may assume multiple configurations (see Fig.2 (a), for example for CuAu) and that the energies of this configurations might be quite close to one other (see Fig.2 (b) for CuAu). The existence of multiple configurations and the fact that they depend on the position of dislocation axis may result in complex variations of dislocation core structure in the process of its motion and under various stress conditions.

2. *Complex evolution of dislocation core structure in a process of motion: model analysis with ab-initio parameterization.*

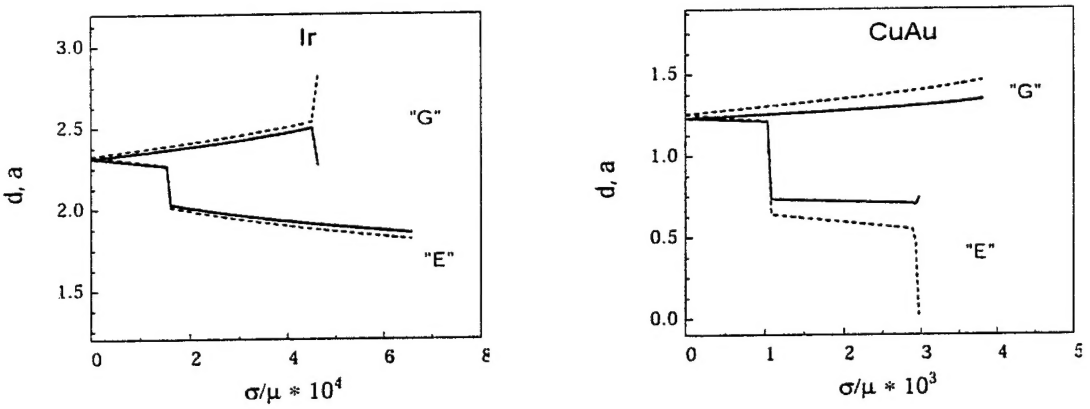

Figure 3: Partials separation d calculated for screw (dashed lines) and edge (solid lines) components of the displacement field of the ordinary dislocation as a function of glide ('G') and Escaig ('E') stresses _ (in units of _, the shear modulus) in fcc Ir and $L1_0$ CuAu.

We recently used this new method to study features of the variation of the dislocation structure under different stress conditions. The effect of the stress has been incorporated as follows

$$E_{tot}(\vec{u}(x)) = E_{el}(\vec{u}(x)) + E_{mis}(\vec{u}(x)) - \int_{-\infty}^{\infty} \sigma_\beta \, u_\beta(x) dx, \qquad (2)$$

where $u_\beta(x)$ is the _ component of the displacement field (_=1 for screw and _=2 for edge components) and _ are the corresponding components of the stress tensor. We have considered two types of stress conditions, glide and Escaig stress (a positive sign is taken to be such as to constrict the partials). The former acts only on the screw component of the displacements and is analogous to the external force acting on the ordinary dislocation center of mass. The Escaig stress on the other hand, influences only the edge component and constricts or expands the partials separation. Results of the calculated stress dependence of the partials separation d (for screw and edge components) for glide ('G') and Escaig ('E') stresses for ordinary dislocations in Ir and $L1_0$ CuAu are presented in Fig.3. As Fig.3 shows, the dislocation core evolves smoothly with increasing glide stress until a critical stress is reached when the dislocation is no longer stable ($\_p$). Results for $\_p$ are summarized in Table 1. Particularly in the case of Ir, the core "relaxation" or adjustment of the core structure to the periodic potential significantly lowers $\_p$ when compared to the "continuum" results. In CuAu, the core "relaxation" effect on the Peierls stress is much less dramatic primarily due to the compensating effect of the transition between competing core configurations.

Table 1: Peierls stress $\_p$ (in units of the shear modulus, _) calculated within the "continuum" (σ_P^{cont}) and discrete (σ_P^{discr}) representation of the misfit energy. Lattice constants a (Å) and a repeat distance in the direction normal to the dislocation line h (Å) for fcc Ir and $L1_0$ CuAu.

	$\sigma_P^{cont}/\_$	$\sigma_P^{discr}/\_$	_ (GPa)	a (Å)	(Å)

Ir	0.002	0.00046	166	3.84	2.35
CuAu	0.008	0.0039	45	3.96	2.42

3. *Superdislocation structure in $L1_2$ intermetallics*

It is well established that superdislocation core structure is the microscopic origin of the anomalous mechanical response in $L1_2$ intermetallics. Existing atomistic calculations of superdislocation structure in some intermetallics suffer from uncertainties in the empirical potential employed. On the other hand, an explanation of why some materials exhibit an anomaly (Ni_3Ge) but others do not (Fe_3Ge) may vary dramatically depending on details of the superdislocation structure.

We used the advantages of our combined *ab-initio-PN* approach to describe dislocation structure starting from accurate electronic structure calculations of GSF energetics to analyze features of superdislocations in $L1_2$ intermetallics. Systematic calculations of GSF surfaces were performed for Ni_3Al, Ni_3Ge and Fe_3Ge intermetallics, a choice dictated by the large amount of experimental data for Ni_3Al and by ongoing experimental measurements in Prof. Hemker's group of the core structure and mechanical properties for $(Ni_xFe_{1-x})_3Ge$ alloys as a function of Fe content.

We found that contrary to what is usually assumed, the set of stacking faults consisting of APB, CSF, and SISF does not provide sufficient information to describe the essential details of superdislocation structure in these materials. In particular, we find that the entire GSF geometry and energetics is important since, for example, the CSF minimum does not exist in Ni_3Ge and Fe_3Ge. We find also that local GSF minima corresponding to APB's are significantly shifted from geometrical positions, and so dramatically affect values of the APB. For example, for Ni_3Ge, the GSF energy at a point corresponding to a hard spheres model the APB is γ_{geom}=600 mJ/m^2, whereas the local minimum corresponding to our *ab-initio* GSF surface is $\gamma_{ab\text{-}initio}$= 410 mJ/m^2. This finding suggests that interpretations of the experimental measurement of dislocation core structures have to be done carefully and within a model (such as PN model) which properly treats the width of finite partials.

For understanding the relation of core geometry and macroscopic mechanical properties in these materials, it is important to determine carefully the splitting path of superdislocations as well as the competition between Shockley and Kear splitting schemes (cf. Fig.4)

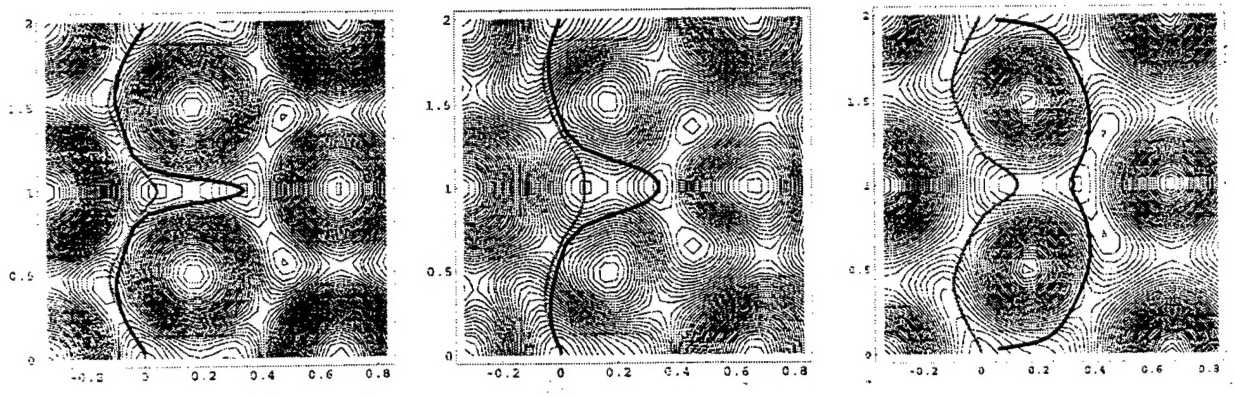

Figure 4: Ab-initio _-surface and the splitting path (dependence of the screw on edge component of displacements) calculated within the PN model determined for Shockley and Kear splitting schemes (gray and black lines, respectively) of superdislocations in $L1_2$ Ni_3Al, Ni_3Ge and Fe_3Ge.

4. *Electronic mechanism of impurity-dislocation interactions in NiAl.*

The electronic structure and energetics of the impurity-dislocation interactions for Ti and V impurities in NiAl were calculated using the first principles real-space tight-binding linear muffin-tin orbital recursion method (TB-LMTO-REC) [4], modeled with the cluster of 20,000 atoms with the coordinates of atoms determined within the PN model as described above. Experiments show that alloying with Ti leads to (i) strong solid solution hardening (SSH) effects [5], and (ii) an increase of the creep resistance [7]. However, the estimates show that the parelastic impurity-dislocation interaction is very small (10^{-2} eV) in Ti and V; therefore, the size-misfit mechanism cannot be responsible for alloying effects.

The impurities were placed in different positions (1-8) near the <100>{010} edge dislocation core in NiAl (Fig. 5 (a)), substituting the corresponding Al atom. The impurity-dislocation interaction energy is shown in Fig.5 (b,c). For most impurity positions, the "repulsion" between the dislocation and impurity takes place during the dislocation glide. However the impurity-dislocation interaction becomes strongly attractive, when the impurity is in position 8. This situation can be characterized as "chemical locking".

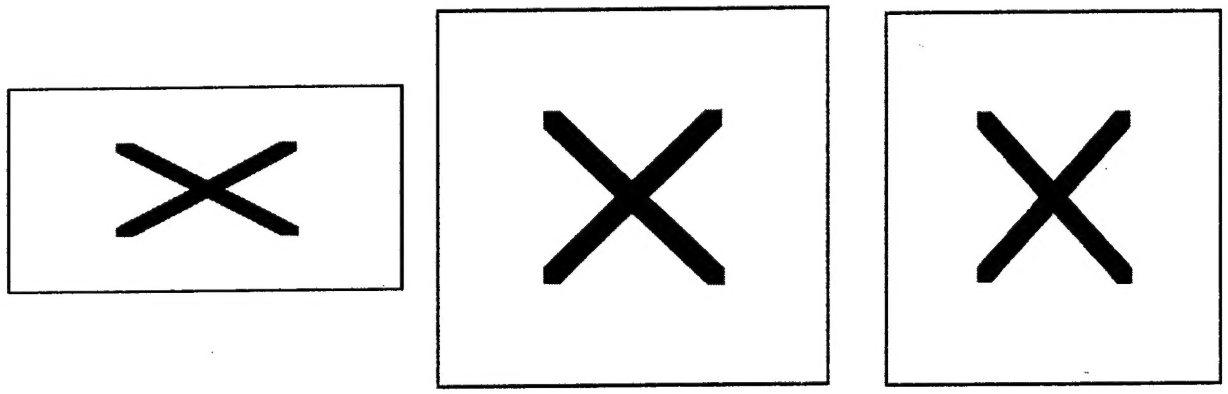

Figure 5: (a) Fragment or the model of the <100>{001} edge dislocation core in NiAl, with substitution impurity positions marked 1-8; (b), (c) impurity-dislocation interaction energy for Ti and V impurities in positions 1-4 and 5-8, respectively.

We analyzed the local electronic structure in the dislocation core and found that the nature of the locking is due to the strong hybridization and preferred bonding between the electronic states of the impurity atom and the localized electronic states appearing in the center of the dislocation core (marked X in Fig. 5) in certain positions during its motion. The one-electron contribution is the main contribution to the impurity-dislocation interaction energy. This is a clear indication that electronic mechanisms are the cause of the impurity-dislocation locking, by the "chemical locking" mechanism.

Another important result obtained is the oscillatory behavior of the impurity-dislocation interaction energy. The central atom of the dislocation core has significant charge excess due to electron localization, causing large charge transfer and long-ranged Friedel oscillations of the

charge density. Thus, the <100> edge dislocation in *bcc* metals and intermetallic compounds represent a unique example of an unusually high "electrostatic locking" interaction, in a contrast to other dislocations where the size of this interaction is very small [6].
The strong impurity-dislocation attraction may influence the macroscopic mechanical properties of NiAl in two ways. First, for the dislocation gliding during the plastic deformation, this relative position will give a local energy minimum; however, more stress will be necessary to move the dislocation further. Hence, this mechanism will contribute to the SSH. Second, for the dislocation at rest, segregation of impurities on the dislocation will occur. Besides SSH, the additions of transition metal impurities can also improve high-temperature properties of NiAl. As an example, Ti additions of the order of 2.5% to 3% result in a 200 to 5000-fold reduction in creep rate in NiAl [7]. Our results suggest that Ti segregation on edge dislocations should play an important role in this effect due to the strongly attractive impurity-dislocation interaction. The mechanism described above can be expected not only in NiAl, but also in other B2 intermetallics where deformations are carried by <100> dislocations (CoTi, CoHf, CoZr), and in *bcc* metals. These findings are important for understanding the nature of the phenomenon of solid solution hardening and the anomalous increase of creep resistance upon alloying in intermetallic alloys.

Future Plans

We plan to investigate:

1) Effect of intrinsic interfaces on fundamental characteristics of mechanical behavior of eutectic composites and coherent two-phase structures:
   a) Cleavage and shear decohesion characteristics of the NiAl/X eutectic composites (X = Mo, W, Cr, Re and V).
   b) Electronic structure effects on lattice misfit parameters of two phase _/_' superalloys NiX-Ni_3AlX (X = Ti, V, Cr, Co, Zr, Re, Ir).
2) Fundamental aspects of dislocation properties and deformation behavior: dislocation structures in homogeneous phases and with intrinsic interfaces.
   a) Dislocation structure and properties of $L1_2$ Ni_3Al and $(Ni_{1-x}Fe)_3Ge$ intermetallics.
   b) Analysis of dislocation structure relevant to a comparison with HREM images.
   c) Multiple core dislocation structures in intermetallics.
   d) Electronic structure effects on the structure of dislocations: role of ternary additions and deviation from stoichiometry.
   e) Incoherent misfit strain: properties of the misfit dislocations.
3) Effect of alloying on the properties of intermetallics
   a) Alloying effect on intrinsic interfaces (APB, CSF, and SISF) in NiAl and Ni_3AI.
   b) Direct total energy calculations of dislocation-impurity interactions.
   c) Fundamentals of the electronic structure of dislocations: glide of dislocations complex dislocation structures (kinks, jogs), and transport properties.

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